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Kinetic thermometric determination of Mo(VI) in vegetables by its catalytic effect on the reaction between hydrogen peroxide and thiosulphate ion

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Abstract

A new kinetic thermometric method for the determination of molybdenum based on the catalytic effect of molybdate ion on the reaction between thiosulphate and hydrogen peroxide in 0.03 M acetic acid is reported. The proposed method is quite sensitive and selective: the linear range of the calibration graph is from 5 to 60 ng ml^{-1}, while the relative standard deviation for 40 ng Mo(VI) per ml is 1.1% ($n = 9$). The presence of foreign ions does not detract from the sensitivity of the method.

The method was applied to the determination of molybdenum traces in various vegetables including dry beans, pumpkin and unpodded peas.

INTRODUCTION

Among kinetic methods, those of a thermometric nature based on catalysed reactions have proved to be highly efficient in the determination of traces and ultratraces of various chemical species. Our past experience in this field [1–4] convinced us that straightforward, affordable instrumentation is more than adequate to determine metal ions at concentrations of a few micrograms per litre, or even less, with a high selectivity. Consequently, thermometric methods make a useful alternative to a number of existing, widely used techniques, e.g. graphite-furnace atomic absorption spectroscopy, inductively-coupled plasma atomic emission spectroscopy, which are much more expensive to set up and maintain.

In continuation of previous research, in this work we developed a kinetic thermometric method for the determination of molybdenum in vegetables based on the catalytic effect of some metal ions on the reaction between hydrogen peroxide and thiosulphate ion [5].

It should be noted that molybdenum is commonly determined using

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other kinetic methods, some of which use photometric detection, e.g. two based on the reaction between H_2O_2 and I^- [6] or rubeanic acid [7]; others rely on the oxidation of various organic compounds with bromate or iodate ion [8], such as that of 1-naphthylamine with bromate [9] or 2-aminophenol with H_2O_2 [10], and the photochemical oxidation [11] or the reaction between Se(IV) and Sn(II) [12]. The detection limit for most of these methods is in the region of 10 ng ml^{-1}.

Other kinetic catalytic methods for the determination of molybdenum use potentiometric detection, e.g. that of Kataoka et al. [13], who employ the I^-–H_2O_2 system and an iodide-selective electrode, or amperometric detection, e.g. that based on the reaction between I^- and BrO_3^- [14].

More specifically, molybdenum in plants is often determined using a method based on the dithiol reaction [15] which was improved by Bingley [16] and Quin and Brosk [17].

Finally, Bradfield and Stickland [18] used the I^-–H_2O_2 system to develop a method for the determination of molybdenum in the range 10–100 ng ml^{-1} (0.1–1.0 ppm in plant material); this was later automated by Quin and Woods [19] using a segmented-flow system.

EXPERIMENTAL

Apparatus

The thermometric set-up used was described in detail elsewhere [20]. It consisted of an adiabatic cell and a 100 kΩ (25°) thermometric thermistor connected to a Wheatstone bridge. The solution was homogenized by means of a propeller stirrer driven by a synchronous motor. In order to minimize noise, the signal from the bridge was passed through an RC filter to an x–t recorder to obtain the thermometric graph, a temperature (T) versus time (t) plot.

The reaction rate was measured thermometrically using the initial-rate method, i.e. by measuring the tangent (dT/dt) in the first linear portion of the thermometric curve.

Reagents

The solutions used included 0.024 M $S_2O_3^{2-}$, prepared from $Na_2SO_3 \cdot 5H_2O$; 0.5 M acetic acid; 0.05 M H_2O_2; and 1.000 g Mo(VI) per l stock solution, made by dissolving 1.8404 g of $Mo_7O_{24}(NH_4)_6 \cdot 4H_2O$ in 1 litre of distilled water. All chemicals used were of analytical reagent grade and distilled water was employed throughout.

Procedure

The solutions were mixed in a 50 ml polystyrene beaker as follows: 25 ml of 0.024 M thiosulphate, 3 ml of 0.5 M HAcO, x ml of an unknown solution or standard to obtain an Mo(VI) concentration between 5 and 60 ng ml, and $(21-x)$ ml of distilled water.

The beaker was then placed in the thermometric cell and the stirrer was started. As soon as a stable recorder baseline, i.e. a stable temperature, was obtained, 1 ml of 0.05 M H_2O_2 was added to the beaker and recording of the kinetic thermometric curve was started, using a scale background of 10 mV and a chart speed of 0.5 cm min^{-1}.

All reactants and the laboratory room were thermostatted at 24.5 ± 0.5°.

The Wheatstone bridge was previously calibrated in order to achieve the maximum possible sensitivity (0.02°C mV^{-1}) at the working temperature.

Procedure for the determination of Mo(VI) in vegetables

The vegetable samples (dry beans, pumpkin and unpodded peas) were carefully weighed and allowed to dry at 100°C overnight. After their moisture content was determined, 10 g of dry product was calcined at 450°C in a muffle furnace for 24 h. The furnace temperature was raised gradually in order to avoid potential losses. Finally, the calcined residue was dissolved in 1:100 HNO_3 to a final volume of 25 ml for each vegetable sample.

In order to avoid any matrix interferences, determinations were carried out by using the standard-addition method.

RESULTS AND DISCUSSION

The experimental variables potentially influencing the performance of the method were optimized by using the univariate method on the basis of the initial rate signal.

Influence of acidity

The effect of the acidity of the medium was investigated by keeping the Mo(VI) and sodium thiosulphate concentrations in the cell constant at 40 ng ml^{-1} and 8×10^{-3} M, respectively. In each experiment, a given amount of acetic acid corresponding to a concentration of 0–0.06 M was added to the cell, which was then made up to a final volume of 49 ml with distilled water. When thermal equilibrium was reached, 1 ml of 0.025 M H_2O_2 was injected into the cell, where its final concentration was thus 5×10^{-4} M.

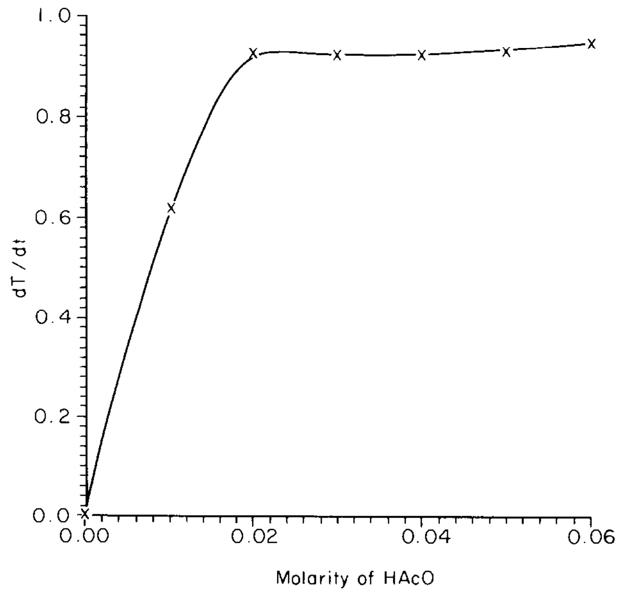

Fig. 1. Variation in the rate of the catalysed reaction with the acetic acid concentration. [Mo(VI)] = 40 ng ml^{-1}; [$S_2O_3^{2-}$] = 8×10^{-3} M; [H_2O_2] = 5×10^{-4} M.

Figure 1 shows the influence of the HAcO concentration on the reaction kinetics under the working conditions used. As can be seen, the reaction rate reached a maximum at an HAcO concentration of 0.02 M, above which it remained virtually constant. We thus chose 0.03 M acetic acid for subsequent experiments.

Reactant concentrations

The influence of the thiosulphate concentration on the reaction rate was studied over the range 2×10^{-3} to 1.6×10^{-2} M at constant concentrations of acetic acid (0.03 M) and Mo(VI) (40 ng ml^{-1}). Once thermal equilibrium was reached, 1 ml of 0.025 M H_2O_2 was injected into the cell. Figure 2 shows changes in the slope of the thermometric curve as a function of the thiosulphate concentration in the presence and absence of molybdenum (the catalyst for the analytical reaction). As can be seen, the slope varied very little above an $S_2O_3^{2-}$ concentration of 1.2×10^{-2} M, which was thus chosen as optimal. We should note that the uncatalysed reaction developed to a negligible extent throughout the concentration range assayed.

The optimal H_2O_2 concentration was determined by keeping the concentration of acetic acid (0.03 M), thiosulphate ion (1.2×10^{-2} M) and Mo(VI) (40 ng ml^{-1}) constant and injecting 1 ml of H_2O_2 solutions containing different concentrations of the peroxide, between 0.010 and 0.2 M. Figure 3 shows the changes in the slope of the thermometric curve as

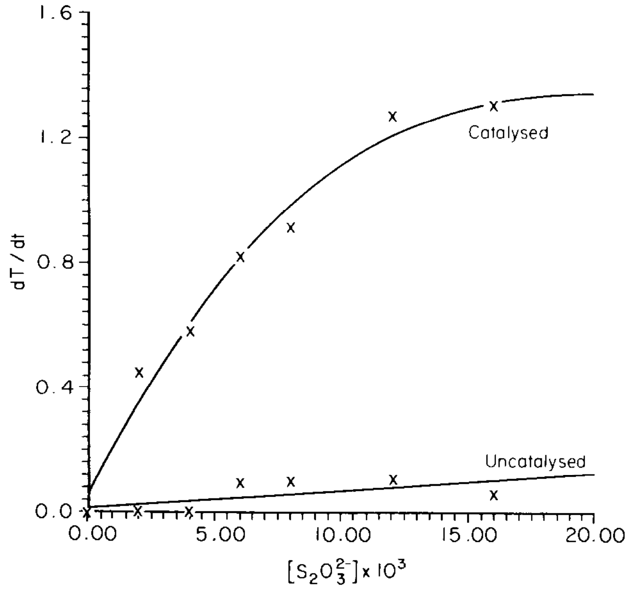

Fig. 2. Variation of the rates of the catalysed and uncatalysed reactions with the sodium thiosulphate concentration. [Mo(VI)] = 40 ng ml^{-1}; [HAcO] = 0.03 M; $[H_2O_2] = 5 \times 10^{-4}$ M.

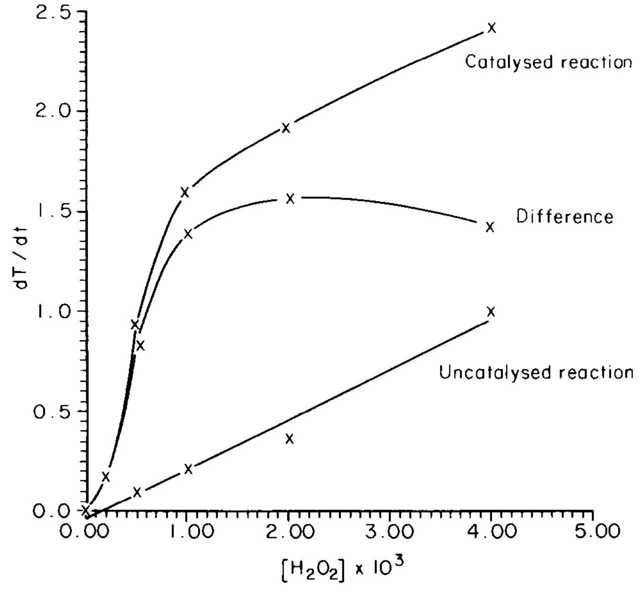

Fig. 3. Influence of the hydrogen peroxide concentration on the rates of the catalysed and uncatalysed reactions. [Mo(VI)] = 40 ng ml^{-1}; [HAcO] = 0.03 M; $[S_2O_3^{2-}] = 1.2 \times 10^{-2}$ M.

a function of the H_2O concentration for the catalysed and uncatalysed reaction, as well as the difference between the two slopes at each hydrogen peroxide concentration. As can be seen, the optimal peroxide concentration was 10^{-3} M (1 ml of 0.05 M H_2O_2); in fact, higher concentrations only increased the rate of the uncatalysed reaction.

Calibration graph and reproducibility

Under the above-described optimal working conditions, we obtained a linear calibration curve between 5 and 60 ng Mo(VI) per ml that conformed to the equation

$$dT/dt = 0.0359[\mathrm{Mo(VI)}] + 0.296$$

where the Mo(IV) concentration is expressed in ng ml^{-1}.

The reproducibility of the method under the optimal conditions was determined using a solution containing 40 ng Mo(VI) per ml. The RSD thus obtained for 9 replicates was 1.1.

Interference

The effect of foreign ions on the determination of Mo(VI) traces by the proposed method was checked by making a set of solutions containing 40 ng Mo(VI) per ml and various potential interferents plus acetic acid and thiosulphate at their optimal concentrations, to which 1 ml of 0.05 M H_2O_2 was injected. Table 1 shows the tolerated limits for the different interferents assayed ($\pm 2\sigma$ of the dT/dt value). As can be seen, the most severe interferences were posed by Fe(III), V(V), and Hg(II). The effect of the first ion can be masked by adding EDTA at a final concentration of 0.05 g l^{-1}, even though this alters the slope of the calibration curve for Mo(VI), which must thus be also run in the presence of the masking agent.

TABLE 1

Tolerated interferent-to-molybdate ratios in the determination of 40 ng Mo(VI) per ml

Ion	[Interferent]/[Mo(VI)]
F^-, SO_4^{2-}, NO_3^-, Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, NH_4^+, Zn^{2+}, Ag^+, Ni^{2+}, Mn^{2+}, Co^{2+}, Cr^{3+}	>100 [a]
Al^{3+}	25
Fe^{3+}	12
Hg^{2+}	5
V(V)	0.5

[a] Maximum concentration assayed.

TABLE 2

Results obtained in the determination of molybdenum and miscellaneous metals in three types of vegetables

Sample	Mg/ (mg g^{-1})	Ca/ (mg g^{-1})	Cu/ (mg g^{-1})	Mn/ (mg g^{-1})	Pb/ (μg g^{-1})	Ni/ (mg g^{-1})	Fe/ (mg g^{-1})	Cr/ (mg g^{-1})	Mo/(μg g^{-1})	
									ICPAES	Kin.-therm.
Pumpkin	86	377	3.2	0.1	–[a]	0.1	2	0.20	1.50[c]	1.40[c]
Beans	499	–[b]	2.1	2.7	–[a]	0.8	11.5	0.14	3.25	3.50
Peas	110	–[b]	1.6	0.8	32	0.9	2.6	0.26	10[c]	11[c]

[a] Not detected. [b] Out of range. [c] Added concentration.

Applications

In order to validate the proposed method, it was applied to the determination of molybdenum in edible vegetables. The procedure used to process the samples was described above. Once mineralized, the samples were analysed by inductively-coupled plasma atomic emission spectroscopy (ICPAES) in order to determine their molybdenum contents, as well as those of potential interferents (Table 2).

No molybdenum was detected in the pumpkin or unpodded pea samples, so they were spiked with the metal ion at the concentrations given in Table 2.

The three types of sample were analysed using the proposed method and the standard-addition technique. As can be seen from Table 2, there was close agreement between the ICPAES results and those provided by the proposed kinetic thermometric method.

CONCLUSIONS

The proposed method for the determination of molybdenum traces is quite sensitive and acceptably selective. Also, unlike other analytical methods used for the same purpose, it can be implemented with simple, inexpensive instrumentation and reagents.

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